Vibrational study of the various forms of (solvated or unsolvated) mobile proton in materials for storage and production systems based on the hydrogen vector. Advantages, limitations and open questions*

Philippe Colomban

Laboratory "from molecule to nano-objects"(MONARIS UMR8233),

Sorbonne Université, CNRS, 4 Place Jussieu, 75005 Paris, France.

The desire to use hydrogen as an energy carrier requires a better knowledge of the materials that can serve as electrolyte or electrode, i.e. solids containing mobile protons. We present here through some examples the contribution and the limits of vibrational spectroscopies (Infrared, Raman and inelastic neutron scattering) to understand the structure and dynamics of proton species and discuss the questions to be resolved.© Anita Publications. All rights reserved.

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1 Introduction

Since the discovery of the 'wandering proton' by Beintema in 1936 in uranium phosphate hydrate (HUP) [1], and then at the end of 1950s in Nafion® poly(perfluorosulphonic acid) membrane developed for the US Gemini orbiter [2,3] the attention paid to the search for solids with high proton conductivity was correlated with variations of oil prices: high just after the first oil crisis in 1975 and then very low until the vogue for ecological themes of the 21st century and subsequent impetus on energy systems based on Hydrogen vector [2]. The objective was to discover stable solids without electron conductivity to be used as electrolyte, or with high electron conductivity to be used as electrode, in a range of temperature making it possible to avoid having to resort expensive electrodes (made of Pt, Pd and Rh) to produce H_2-air fuel cells, water electrolyzers and converters of CO_2 into useful chemical compounds or, simply H-sensors [3-6]. Academic works on the optimization of materials synthesis and measurements of conductivity are the most frequent, although often carried out under conditions that are not very representative of those required by the technical and economic constraints (temperature range, 20-50 bar gas pressure, high current per surface unit) [6-8]. Attempts to understand the nature of protons, especially mobile ones, is much more limited, especially in recent years. However, from the first studies such as the Ensberger review in 1983 [9] or the first book devoted to Proton Conductors [3], the uniqueness of the proton was underlined. A recent review paper reports the state-of-the-art concerning the understanding of the nature of the chemical bond between the proton in the solid phase and its dynamics in the working temperature range, for temperatures between 250-450, 750-1000 or even 1200 K depending on the type of application [10] and a summary is given here.

2 How to highlight the presence of protonic species

Four methods are effective: Thermo-Gravimetric Analysis (variation of mass with temperature), incoherent neutron scattering (Elastic and Quasi elastic scattering, diffraction background), vibrational spectroscopy (Infrared, inelastic neutron and Raman scattering) and electrochemical evidence (production

of H_2, etc.) [3,10,11]. The temperature at which the departure of protons or water (or NH_3) occurs gives information on the strength of the bond between the proton and its environment, typically around 400-450 K for the departure of water molecules, 700 K for de-hydroxylation or even more than 1000 K for some isolated protons [11]. Due to the very large value of the incoherent section of the H isotope, 80 b, i.e. 100 times more than for most other elements [12], the incoherent spectrum of a compound containing a little amount of H corresponds to the modes involving proton displacement. The comparison of the signal of a compound before and after drying at ~ 400K makes it possible to differentiate the contributions of bulk and surface protons [11]. The use of perfectly densified single crystals or ceramics – and not powder – guarantees the quality of the results, whether for diffraction or neutron spectroscopy [13-15]. Due to its very polarizing nature, the proton species form dipoles and, therefore, infrared spectroscopy is the most effective method to study protonic species [3,10,16,17]. On contrary, as the number of electrons involved in the M-H bonds is very low, the Raman spectra are not very intense but the proton strongly disturbs the structure hosting protons and this modifies the Raman signatures of the host lattice. Different procedures exist to obtain an infrared spectrum. The only ones that minimize the reactions between the sample and the environment (the small temperature difference between the solidification point of water and its boiling point leads to a large variation in the partial pressure of water and the formation of a strong gradient at the surface of the compounds, modifying the composition and local crystallinity) are the use of single crystals, dense ceramics or powders encapsulated in liquid paraffin (Nujol®, Fluorolube®) to control the partial pressure of water. The later procedure allows to avoid reaction with NaCl, KBr or even CsI wafers. Only CaF_2, KRS5® and Si wafer are reliable. Transmission measurements should be preferred by DRIFT and ATR-FTIR techniques. In these two techniques the spectrum is dominated by surface water and hydroxy (carbonate) species [10]. Deuteration (or ^{3}T isotopic substitution), H/D isotopic dilution and partial ion exchange procedures are very useful to 'simplify' the spectrum and its assignment [10,18].

3 The well established protonic species

At least three types of 'protons' are considered, characterized mostly using vibrational spectroscopy [2,6-8]: (i) covalently –bonded proton, (ii) isolated or ionic proton and (iii) delocalized proton without visible signature.

In the first type, the proton establishes covalent bond with one acceptor ion, oxygen (OH, HO-H_2), nitrogen (HN-H_3), or sulfur (H-SO_4) [2-6]. These different species, namely hydroxyl ions (OH⁻), oxonium (H_3O^+) /ammonium (NH_4^+) ions, more solvated hydroxonium ions ($H_5O_2^+$, $H_7O_3^+$, etc.), etc. present clear signatures in infrared spectroscopy [16-19], which are all the more characteristic – and visible – when the X-H…Y bond is not too strong [3,6]. Figure 1 shows typical Infrared signatures recorded on β alumina.

4 New proton species

Inelastic incoherent neutron spectroscopic signatures recorded on a layer of oriented fully hydrated and oxonium β alumina single crystals are presented in Fig 2 [20]. The dominant species are oxonium and hydroxonium ions, respectively and the spectra confirm the assignments made from infrared analysis [16-19]. However, the behavior of the H_3O^+ ion is strange, the simulation of the spectrum is the best if we consider an ion with Td symmetry; i.e. with a partial distribution of the protons around the oxygen ion [20].

Note the large continuous background which indicates that not all the hydrogen atoms are engaged in covalent bonds. Indeed, because of its low mass, if the proton is not (significantly) bound, the proton recoils and gives rise to large continuous background, observed for all proton conductors [20-26] as well on other materials such as carbon and manganese oxide.

The obtained INS (Inelastic Neutron Scattering) spectra of compounds, where the infrared spectra identify oxonium and hydroxonium ions provide exceptional information; for instance. Keggins salts (also

called POMs: polyoxymetallates) which have been extensively studied [24,25], with well-established structures by both X-ray and neutron diffraction, presents many hydration states and in particular oxonium and hydroxonium species. In fact, different forms are in a dynamic equilibrium depending on the temperature [3,9].
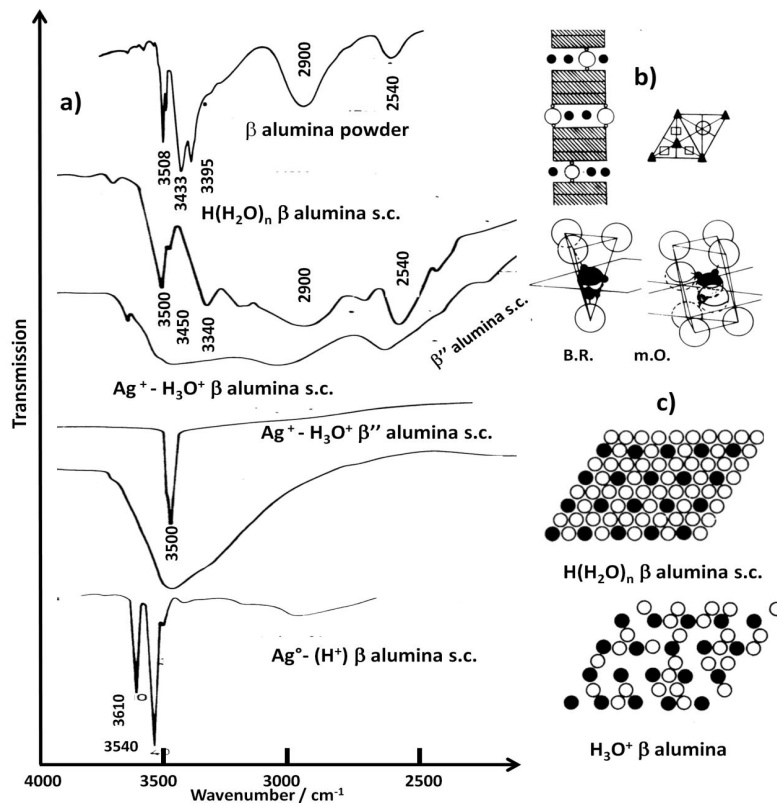

Fig 1. Representative IR signatures of O-H, H_3O^+ and $H_5O_2^+$/$H_7O_3^+$ species in β alumina (a), schematic of the structure (b, with view of the Beever–Ross and middle-oxygen sites; black circle: oxonium ion; open circle: oxygen ion) and sketch of the site occupation in the conducting plane. In a), from the top spectra recorded using a dispersion of powdered partially hydrated oxonium β alumina single crystal in fluorolube® mull in-between two CaF_2 wafers, comparison between the spectra of single crystal of β and β" alumina phase, comparison of the spectra of single crystal of oxonium β and β" alumina after partial ion exchange of ~30% of oxonium ions with silver ions [19]. Reliable relationship established between vibrational parameters (center of gravity of stretching band, bandwidth) and crystallographic data (O-H...X donor-acceptor distance) [16] allows determination of the H-bond distance with neighboring proton acceptors [10,19]. c) sketch of the conductive plane filling with water molecules to complete the packing of the oxygen ion layer.

Whatever be the compound hosting oxonium or hydroxonium ions, the INS spectra are very similar to those obtained on the β aluminas, but for the almost dehydrated Keggins salt compound a very simple, unexpected spectrum is obtained: the spectrum consists of a single peak at 1150 cm^{-1} and its harmonics, characteristic spectrum of an 'isolated' proton, ionic, or polaronic in its site. It is the second type of proton.

5 Nominally anhydrous proton conductors

The search for materials used as solid electrolyte in fuel cells and then electrolyzers led in the 1960s to identify perovskites as proton conductors at medium temperature [3,10]. Due to the possibility of creating oxygen vacancies perosvskites are high temperature anionic conductors. Different researchers used these materials as electrolyte or after substitutions generating electronic conductivity as electrode of industrial

prototypes. But the hydrogen content is very weak on the order of doping level in semiconductors. Indeed, it appears that only part of the oxygen vacancies created by partial substitution of zirconium (4^+ ion) by 3^+ ions (cerium, yttrium, erbium...) are filled in the presence of water vapor.
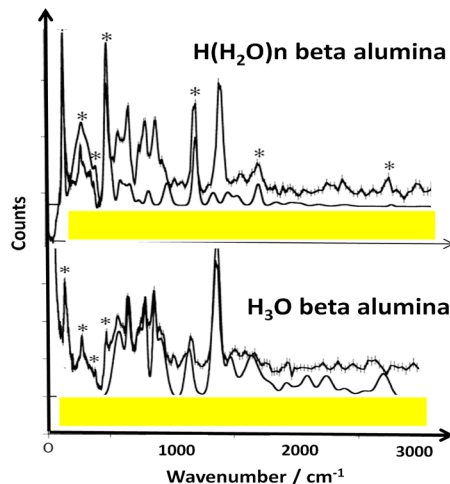

Fig 2. Representaive Inelastic (incoherent) neutron spectra of fully hydrated (top) and partly dehydrated beta alumina (bottom) (redrawn from ref [20]). Simulation of the spectrum for $H_5O_2^+$ and H_3O^+ ions are given. Note the strong background (colored in yellow).

Figure 3 compares the Raman spectra of a dense ceramic of $SrZr_{0.9}Er_{0.1}O_{3-\delta}$ as a function of heat treatment sequence cycles (from RT to 900°C under ultra-high vacuum, i.e. de-protonation) and autoclave protonation (500°C, 40 bar H_2O, several days to protonate to core) [14]. The bulk proton content is measured by TGA, elastic neutron scattering and neutron diffraction [10,11]. If the densification of the ceramic is less than 95%, the quantity of proton species formed on the surface of the ceramic becomes much greater than the quantity inserted. In this case. an infrared spectrum corresponding to strontium hydroxycarbonates (or barium for homologues) is observed. For a denser ceramic, no spectrum is detected either by infrared or by incoherent inelastic neutron scattering [10,14], which is understandable given the low hydrogen bulk content (e.g. $H_{0.02}SrZr_{0.9}Er_{0.1}O_{3-\delta}$). On the other hand, as illustrated in Fig 3, protonation modifies the crystal lattice (symmetrization, the distortion of the ideally cubic perovskite lattice is reduced), the phase transition sequences and the Raman spectrum in the 700-900 cm^{-1} range where are presents the Zr-O elongation modes perturbed by the presence of nearby vacancies [14]. The changes in the spectral signature of these modes is evident while the rest is unchanged. In particular, the lattice modes below 200 cm^{-1} are unchanged because the structure is unchanged, which is confirmed by neutron diffraction, only the parameters are slightly modified: the volume of the unit-cell contracts from 278 to 277 A^3 after protonation, which proves the disruption induced by the 0.02 H inserted. We see the effectiveness of Raman analysis to detect disturbances of the host lattice while proton species cannot be detected.

6 Open questions and perspectives

This quick summary of the vibrational signatures concerning the species of mobile protons in the solid phase makes it possible to formulate questions and highlights the imposing need to be able to work on single crystals and to go to the fundamental questions. The symmetry of the oxonium ion in beta alumina or the presence of the continuous background in neutron INS (the widely studied compounds) present points to be clarified. The quantum behavior of the proton and possibilities of its correlations (Quantum entanglement) remain to be studied in many compounds [28,29]. If we remember that the size of the proton is just halfway between that of the lithium ion and the electron, we understand that the understanding of the modification of
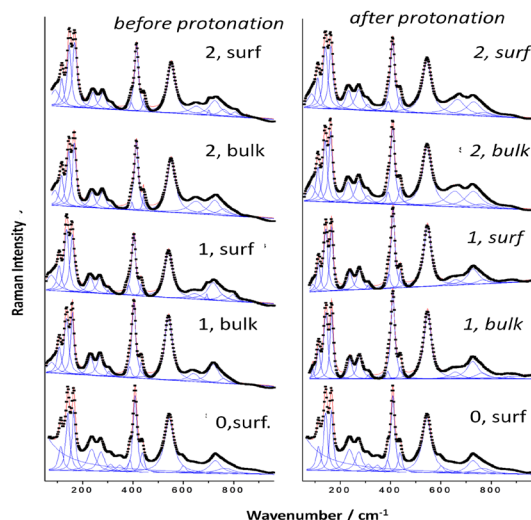
Fig 3. Comparison of Raman spectra recorded on a dense sintered $SrZr_{0.9}Er_{0.1}O_{3-\delta}$ ceramic (>98% of the theoretical density), at the surface (surf) and in the core after breakage (bulk) before protonation with those recorded after protonation in an autoclave at 500°C under 40 bar H_2O for a few days. The composition of protonated ceramic is $H_{0.02}SrZr_{0.9}Er_{0.1}O_{3-\delta}$ [14].

the properties and the structure by a doping (a few % of the oxygen vacancies possible are only concerned) requires fine studies on single crystals. The use of powder does not allow precise analyses due to the contribution of surface protonated species. The work on perfectly densified ceramics cannot really replace the analysis of single crystals. Thus for perovskites, it is necessary to identify which types of vacancies and how can be filled by oxygen ions and protons. This can only be done from single crystals. The study of the role and behavior of grain boundaries will be a second step. Isotopic substitutions (H/D/T) and ion exchanges provide important experimental clarifications and they make it possible to differentiate static and dynamic disorders by measurements over a wide temperature range. The study of conductivity in the whole frequency range from DC to THz is necessary [30] to understand the dynamics of the proton and its scattering mechanism [31,32]. As from the technical-economic point of view, systems such as fuel cells, electrolyzers and converters of CO_2 into valuable products must be pressurized (20 to 50 bar, typically), studies *in situ* or operando in autoclave must be made.

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